The effects of electrolyte concentration in the emulsion polymerization of styrene

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(*Received* 7 *November* 1981)

Using concentrations below that required to coagulate the latex, the effects of the addition of potassium chloride on the emulsion polymerization of styrene have been investigated. When potassium decanoate (an emulsifier with a high critical micelle concentration (*c.m.c.*)) is used the increase in the concentration of micellar emulsifier and the decrease in the area occupied by an emulsifier molecule at the polymer/water interface are significant. When this is taken into account Gardon's equation for latex particle size reproduces the trend of the experimental results at the lower electrolyte concentrations. The agreement can be made quantitative by choosing alternative values for the propagation rate constant of styrene and the rate of radical formation from persulphate. With potassium octadecanoate (which has a low *c.m.c.*) and with potassium decanoate at the higher electrolyte concentrations these factors cannot account for the results observed.

Keywords Electrolyte emulsion polymerization; Gardon's equation; latex; particle size; styrene

INTRODUCTION

Electrolytes may be included in emulsion polymerization recipes either coincidently (as an impurity in the emulsifier) or deliberately (to reduce the latex viscosity or to lower the freezing point of the aqueous phase). Blackley[1] has summarized most of the information published before 1973 on the effects of electrolytes in emulsion polymerizations. The effect of ionic strength is not taken into account explicity in the theories of emulsion polymerization of Smith and Ewart[2] or Gardon[3] although Gardon's own experiments show that addition of sodium sulphate (in concentrations up to 0.30%) causes a significant increase in the size of polymethyl methacrylate latex particles (from a diameter of 126 nm to 165 nm). Subsequently Klein, Kuist and Stannett[4] working with vinyl acetate and Goodwin, Ottewill, *et al.*[5] using styrene without an emulsifier have recognized the ionic strength as a factor affecting the results obtained in emulsion polymerizations. It is, of course, well known that colloid stability is affected by ionic strength.

Several effects of an increase in electrolyte concentration in an emulsion polymerization system can be foreseen: (1) a decrease in the critical micelle concentration (*c.m.c.*) of the emulsifier with a consequent increase in the concentration of micellar emulsifier, (2) an increase in the amount of emulsifier adsorbed on latex particles so that the area, a_S, per molecule at the interface decreases, (3) an increase in the size of the emulsifier micelles, (4) an increase in the amount of monomer solubilized in micelles, (5) a change in the effective charge on micelles and latex particles, i.e. a change in the extent of counterion binding. Sufficiently large electrolyte concentrations will destabilize electrostatically stabilized lattices and cause them to coagulate or coalesce but it is possible to study the effects of electrolyte additions over a range of concentrations below the critical coagulation concentration of a latex.

Two pure alkyl carboxylate emulsifiers were used: potassium decanoate which has a comparatively high *c.m.c.* and potassium octadecanoate which has a low *c.m.c.*

EXPERIMENTAL

Polymerizations

The emulsifiers were prepared *in situ* by neutralizing the specially pure acid (B.D.H. better than 99% by g.l.c.) with enough aqueous potassium hydroxide solution to leave an excess of 0.016 mol dm^{-3} KOH to prevent hydrolysis (pH approx. 11.5). Styrene was redistilled before use. The initiator, potassium persulphate, was recrystallized. The polymerization vessel was a 500 cm^3 five-necked flask fitted with a stirrer and a double-surface condenser. A stream of pure nitrogen was passed through the monomer and the water before emulsification to remove oxygen. An atmosphere of nitrogen was maintained over the emulsion during the polymerization. The nitrogen (British Oxygen Co. Ltd. 'Oxygen-free') was passed through alkaline pyrogallol solution to remove residual oxygen.

Critical micelle concentrations

Surface tensions of emulsifier solutions were determined at 50°C over a range of concentrations by the Du Nouy ring method using a torsion balance manufactured by the White Electrical Instrument Co. Ltd, Malvern Link.

Adsorption areas

The area, a_S, occupied by an emulsifier molecule at the polymer/water interface can be determined by adding a solution of the emulsifier to a latex of known particle size which contains a known amount of the same emulsifier

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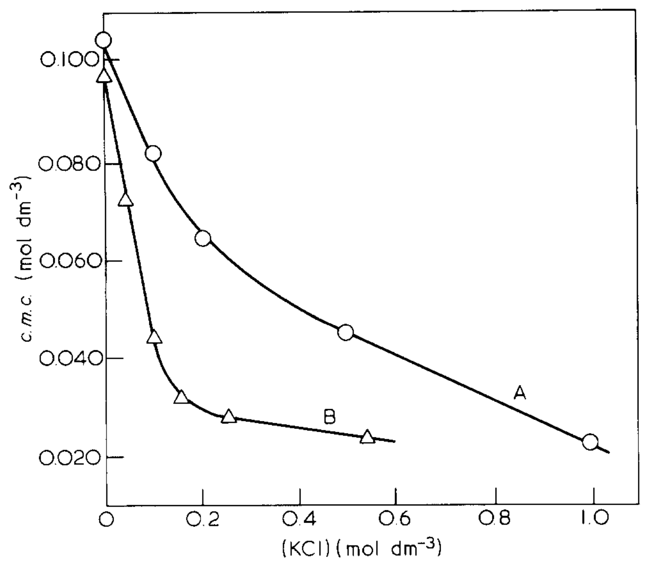

Figure 1 Effect of electrolyte concentration on the critical micelle concentration of potassium decanoate at 50°C (A) Kolthoff and Stricks's results obtained by dye solubilization[8] (B) present work using Du Nouy method measuring adsorption saturation at the air/water interface

until the *c.m.c.* is reached in the solution. When an emulsifier with a high *c.m.c.* is studied it is essential to correct for the dilution of the latex by the solution added[6].

Particle sizes

Average latex particle sizes were determined using a Brice–Phoenix Series 1000 Light Scattering Photometer by the procedure of Burnett, Lehrle, *et al.*[7]: a computer curve fitting programme was used to facilitate extrapolation to zero angle. This procedure gives two particle size averages, $\bar{d}_\tau$, the diameter of a particle with the weight-average mass, and $\bar{d}_{LS}$.

$$\bar{d}_\tau = \sqrt[3]{\frac{\Sigma n_i d_i^6}{\Sigma n_i d_i^3}} \qquad \bar{d}_{LS} = \sqrt{\frac{\Sigma n_i d_i^8}{\Sigma n_i d_i^5}}$$

Of these averages, $\bar{d}_\tau$ is the more reliable but $\bar{d}_{LS}$ is useful for giving an indication of the dispersity of particle size. When the sample is not monodisperse ($\bar{d}_\tau \neq \bar{d}_{LS}$), $\bar{d}_\tau$ is larger than the root-mean-cube diameter $\bar{d}_{rmc} = \sqrt[3]{\Sigma n_i d_i^3/\Sigma n_i}$ which is the average required[3] for calculation of N, the number of latex particles per unit volume or of the root-mean-square diameter $\bar{d}_s = \sqrt{\Sigma n_i d_i^2/\Sigma n_i}$ i.e. the diameter of a particle with the average surface area which is the average required for the calculation of the adsorption areas, a_S, of emulsifiers. Consequently N_τ calculated from $\bar{d}_\tau$ is too small. The adsorption area, a_τ, calculated from N_τ and $\bar{d}_\tau$ is also low. To enable the magnitude of these errors to be assessed all the particle size averages were calculated from electron micrographs of one sample.

RESULTS

Critical coagulation concentrations

In order to establish that the highest concentrations of added electrolyte were not large enough to cause the coalescence of monomer swollen latex particles, a latex prepared with the standard concentrations of potassium decanoate (0.128 mol dm^{-3}) and persulphate (7.4×10^{-3} mol dm^{-3}) was short-stopped at 60% conversion by addition of *p*-benzoquinone. One portion of the latex was diluted with an equal volume of distilled water and another with an equal volume of 0.500 mol dm^{-3} KCl solution. Both were left for 15 h in a thermostat at 50°C. The average particle diameters $\bar{d}_\tau$ were then measured as 78.8 nm in absence of post-added electrolyte and 79.6 nm in presence of 0.250 mol dm^{-3} KCl. Thus it appears that coalescence should not be a factor in polymerizations below this concentration of potassium chloride. Lattices prepared in presence of 0.750 mol dm^{-3} KCl were stable.

At the standard concentration of potassium octadecanoate used (8.05×10^{-3} mol dm^{-3}), KCl concentrations in excess of 0.100 mol dm^{-3} induced coagulation during the polymerization but, apart from some slow sedimentation, lattices prepared at lower electrolyte concentrations remained stable for several months.

Critical micelle concentrations

Figure 1 shows the dependence of *c.m.c.* on potassium chloride concentration obtained by the surface tension method and similar results published by Kolthoff and Stricks[8] who used the dye solubilization method. Although the results obtained in the absence of added electrolyte agree well there is a large difference in the results obtained in presence of potassium chloride.

The use of a solubilizate may induce a change in the *c.m.c.* but Kolthoff and Stricks obtained similar results with three different dyes: a logarithmic plot of their results against the total counterion concentration is linear with a slope of −0.55. The present results were obtained primarily as calibration curves for the soap titration method of determining a_S: they do not yield a linear logarithmic plot. The Du Nouy method actually measures adsorption at the air/water interface and although it has generally been assumed that the concentration at which the air/water interface becomes saturated with surfactant is the same as that at which micelles are formed in solution it now seems that this assumption is not always justified. Discrepancies between results obtained by different methods in different laboratories may be attributable to differences in the purity of the samples studied but Urban[9] has recently published results obtained on the same sample showing that results obtained by the Du Nouy ring method (measuring adsorption at the air/water interface) and by the conductivity method (measuring association of ions in the bulk of the solution) differ. Since it is the micellar concentration in the bulk of the solution which is relevant for emulsion polymerization, Kolthoff and Stricks' results have been preferred for the calculation of micellar emulsifier concentrations.

Particle size

Table 1 shows that the size of the latex particles finally obtained in the experiments with potassium decanoate initially decreases with increasing electrolyte concentration but that it passes through a minimum at 0.25 mol dm^{-3} KCl and increases slowly at higher electrolyte concentrations. The initial decrease in particle size is mainly a consequence of an increase in the concentration of micellar soap as a result of the decrease in *c.m.c.* although this increase is partially compensated by a decrease in a_S. When these factors are taken into account the particle size calculated from Gardon's equation is parallel to the observed results. Invocation of an enhanced rate of initiator decomposition would serve

Table 1 Effect of electrolyte addition on the size of polystyrene latex particles produced using 0.128 mol dm^{-3} potassium decanoate and 7.40 x 10^{-3} mol dm^{-3} potassium persulphate at 50°C

(KCl) (mol dm^{-3})	Micellar soap (mol dm^{-3})	a_S (Å^2)	$\bar{d}_{rmc}$ (nm) Experimental	$\bar{d}_{rmc}$ (nm) Gardon
0	0.024	70.0	75.6	91.8
0.050	0.036	63.4	71.6	86.5
0.063	0.039	–	70.4	–
0.125	0.052	61.3	65.9	83.0
0.250	0.068	59.7	63.6	78.7
0.455	0.081	–	65.4	–
0.530	0.085	–	66.5	–

Table 2 Effect of electrolyte addition on the size of polystyrene latex particles produced using 8.05 x10^{-3} mol dm^{-3} potassium octadecanoate and 7.40 x 10^{-3} mol dm^{-3} potassium persulphate at 50°C

(KCl) (mol dm^{-3})	Micellar soap (mol dm^{-3})	a_S (Å^2)	$\bar{d}_\tau$ (nm) Experimental	$\bar{d}_{rmc}$ (nm) Gardon
0	0.00750	29.7	101.0	105.2
0.020	0.00764	(28.0)	107.2	107.5
0.050	0.00772	26.5	134.0	110.0
0.075	0.00777	(25.8)	153.0	111.0
0.100	0.00782	25.2	165.0	111.5

to bring the calculated values into close agreement with the observed values for KCl concentrations below 0.250 mol dm^{-3}.

By contrast, *Table 2* shows that the final latex particle diameter increases monotonically with electrolyte concentration in the experiments with potassium octadecanoate as emulsifier. In this case the effect of the change of *c.m.c.* and the adsorption area of a surfactant molecule with electrolyte concentration is minor.

The particle size distribution of one latex prepared at 60°C with potassium octadecanoate is shown in *Figure 2*. 600 particles were measured. The distribution is quite narrow. Averages were calculated as: number-average $\bar{d}_n = \Sigma n_i d_i / \Sigma n_i = 87.7$ nm, $\bar{d}_s = 88{,}65$ nm, $\bar{d}_{rmc} = 89.5$ nm, $\bar{d}_{sv} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2 = 91.0$ nm, $\bar{d}_\tau = 93.0$ nm, $\bar{d}_{LS} = 106.6$ nm. The experimental values from light scattering were $\bar{d}_\tau = 89.7$ nm, $\bar{d}_{LS} = 140.0$ nm. On the assumption that particle size distributions of all samples would be similar, an estimate of $\bar{d}_{rmc}$ may be obtained by reducing the experimental value $\bar{d}_\tau$ by 3.76%. N_τ (calculated from $\bar{d}_\tau$ instead of $\bar{d}_{rmc}$) would be expected to be 11% low and a_τ (i.e. a_S calculated from N_τ and $\bar{d}_\tau$ instead of N and $\bar{d}_s$) would be expected to be 2.3% low also. However N and a_S should follow the same trends as N_τ and a_τ so long as changes in electrolyte concentration do not change the form of the particle size distribution.

It is probable that the increase of particle size with electrolyte concentration has a common cause in both cases. This may be the increase in the size of the emulsifier micelles with electrolyte concentration but unfortunately no data are available to substantiate this idea.

Polymerization rates

Conversion-time curves were determined at 60°C gravimetrically. The curves obtained in the experiments with potassium decanoate (*Figure 3*) are of the normal form for emulsion polymerizations but it is notable that the duration of Interval I (the interval in which latex particles are nucleated) diminishes as the electrolyte concentration is increased. Although this would be expected to result in narrowing the particle size distribution, the Interval II rate is directly proportional to N_τ so that the N_τ/N ratio cannot have changed significantly. Increase of electrolyte concentration also prolongs the duration of Interval II: this could be a result

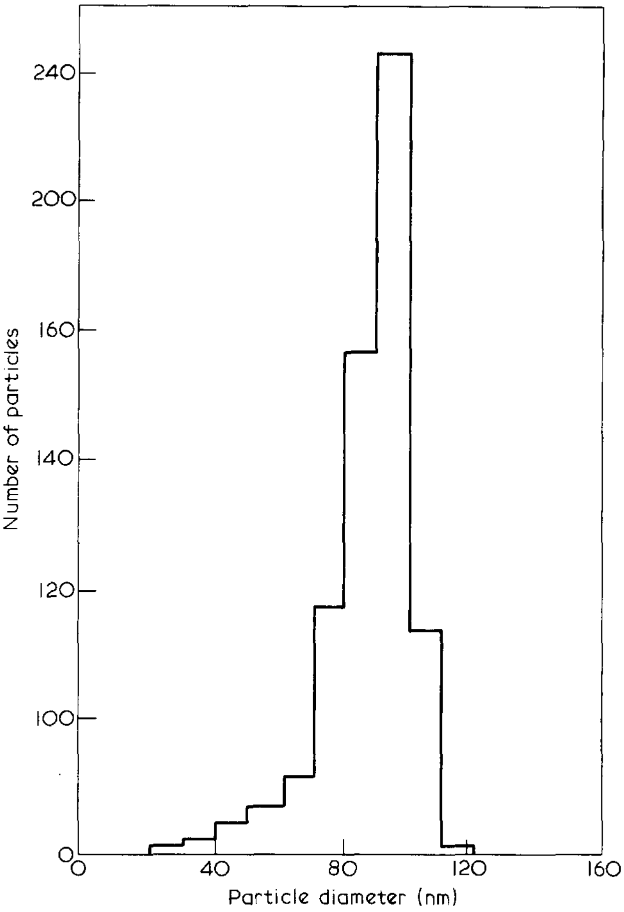

Figure 2 Particle size distribution histogram of a polystyrene latex prepared at 60°C with 8.27 x 10^{-2} mol dm^{-3} potassium octadecanoate as emulsifier and 5.55 x 10^{-3} mol dm^{-3} potassium persulphate as initiator

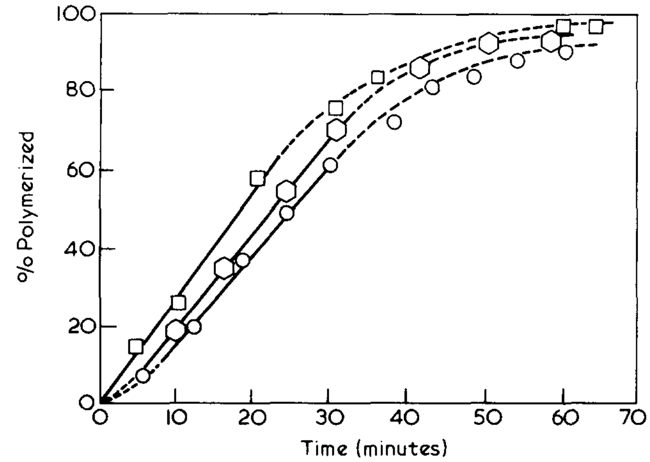

Figure 3 Conversion–time curves for the polymerization of styrene at 60°C emulsified with 0.128 mol dm^{-3} potassium decanoate. Initiator, potassium persulphate, 7.40 x10^{-3} mol dm^{-3}. ○, No added electrolyte, ⬡, KCl 0.050 mol dm^{-3}, □, KCl 0.500 mol dm^{-3}. Solid lines indicate the duration of Interval II

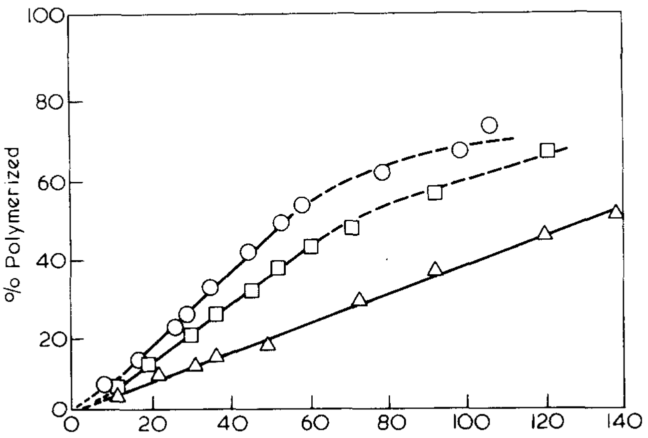

Figure 4 Conversion–time curves for the polymerization of styrene at 60°C emulsified with 8.05×10^{-3} mol dm^{-3} potassium octadecanoate. Initiator, potassium persulphate, 7.40×10^{-3} mol dm^{-3}. ○, No added electrolyte, □, KCl 0.020 mol dm^{-3}, △, KCl 0.050 mol dm^{-3}. Solid lines indicate the duration of Interval II

of the increase of interfacial tension because of the electrolyte addition. According to the Morton–Kaizerman–Altier equation[10] an increase in interfacial tension would decrease the equilibrium monomer concentration in the latex particles which would permit the monomer droplets to persist longer.

The conversion-time curves with potassium octadecanoate (*Figure 4*) are abnormal. Although the final latex was stable, the unusual form of the curves could be a result of particle coalescence during the polymerization. The total amount of emulsifier present in these experiments was low and it would be desirable to obtain some further results at a higher emulsifier concentration.

DISCUSSION

The condition for the cessation of latex particle formation used by Smith and Ewart[2] and by Roe[11] and maintained by Gardon[3] is that the latex particle surface should have increased sufficiently to adsorb all the emulsifier. Consequently it would be expected that when equal molar concentrations of different emulsifiers which have the same value of a_S are used equal numbers of latex particles would be formed giving equal rates of polymerization during Interval II. This is not what is observed. When equal total concentrations of sodium alkyl sulphates are used[12] the number of latex particles formed and the Interval II rates increase with the length of the alkyl chain. According to the older literature[13] all sodium alkyl sulphates have the same value of $a_S = 52$ Å^2 but this conclusion was based on measurements at the air/water interface and Smith and Ewart's assumption that the area occupied by a surfactant molecule is the same in a micelle or at the air/water or polymer/water interface at the *c.m.c.* in solution. This assumption is not justified. The value of a_S varies with the polarity of the polymer on which the emulsifier is adsorbed[14,15,16] and with temperature, electrolyte concentration, and degree of swelling of the polymer[16]. Moreover when results are obtained for the polystyrene/water interface[16], a_S is found to decrease with increasing alkyl chain length in the sodium alkyl sulphate series just as was found earlier[17] for the potassium alkyl carboxylates. The increase in N and Interval II polymerization rate is attributable to the increase in the concentration of micellar emulsifier as the *c.m.c.* decreases with increasing alkyl chain length. With styrene above the *c.m.c.* of the emulsifier micellar nucleation of latex particles is dominant. Consequently N depends on the micellar emulsifier concentration rather than the total emulsifier concentration. When equal micellar concentrations are used, N (and the Interval II rate, R_p) might be expected to decrease as the alkyl chain length increases because

$$R_p \propto N \propto (a_S S)^{0.6}$$

where S is the emulsifier concentration. In fact all members of both the sodium alkyl sulphate and potassium alkyl sulphate series produce the same number of latex particles giving the same Interval II polymerization rates when used at equal micellar concentrations[18]. It therefore appears that the correct condition for the cessation of particle formation has not been used despite the fact that, when the values of the constants which he recommends are used, Gardon's equations do give good results for the size of particles formed and the rate of styrene emulsion polymerizations[19], particularly when the micellar rather than the total emulsifier concentration is used for emulsifiers with a high *c.m.c.* for which these concentrations differ significantly.

Although Gardon's[3] equations do not provide explicitly for an effect of ionic strength it is possible that changes in the concentration of micellar emulsifier and in the value of a_S could account for the changes in particle size which are observed. *Table 1* and *Figure 2* show that the correct trend is, in fact, obtained in the case of potassium decanoate at the lower electrolyte concentrations. If the value of the propagation rate constant for styrene $k_p = 123$ dm^3 mol^{-1} s^{-1} is used the agreement between calculated and observed values is nearly quantitative. However although this value[20] has been widely quoted it does now seem that it may be too low. Hawkett, Gilbert and Napper[21] have recently concluded that the value should be much higher (258 dm^3 mol^{-1} s^{-1}). It was not originally realized that the mutual termination of polymer radicals is a diffusion controlled reaction so that the rate constant, k_t, decreases when the viscosity of the solution increases as polymer is formed. O'Driscoll[22] has shown that a major cause of the discrepancies between published values of polymerization rate constants is that they rely on a combination of the values of $k_p/k_t^{1/2}$ and k_p/k_t determined under different conditions in which the values of k_t are actually different! Using a technique devised to overcome this difficulty (Spatially Intermittant Polymerization), Mahabadi and O'Driscoll[23] have determined k_p for styrene over the temperature rante 15°–30°C: the Energy of Activation is 30.0 kJ mol^{-1} in good agreement with values found by other workers. Extrapolation of their results gives $k_p = 190$ dm^3 mol^{-1} s^{-1} at 50°C. This is probably the best value available at present and is the value used for the calculations in *Table 1*. Taking $a_s = 70$ Å^2, the calculated value for the diameter of the latex particles formed with potassium decanoate without added electrolyte id $\bar{d}_{rmc} = 86.5$ nm (using Matheson's[20] value for k_p), 91.7 nm (as given in *Table 1* using Mahabadi and O'Driscoll's value[23]), and 94.5 nm (using Hawkett's value[21]).

Further there is an increasing body of evidence which indicates that the value for the decomposition rate

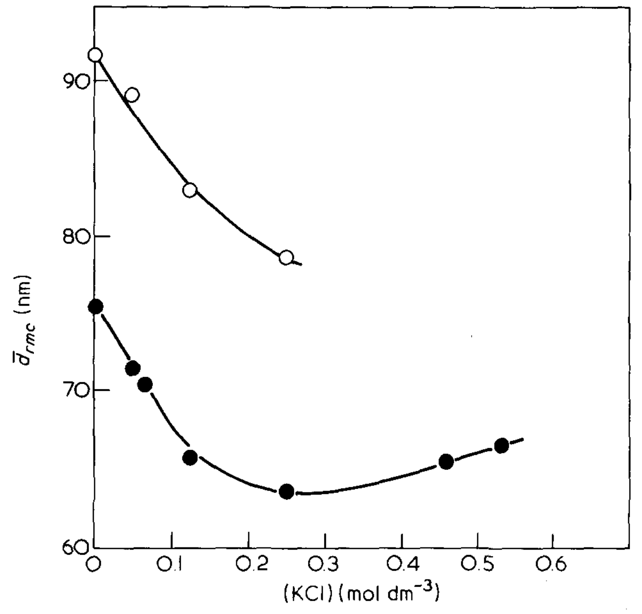

Figure 5 Dependence of the diameter $\bar{d}_{rmc}$ of a particle of average volume on electrolyte concentration in the polymerization of styrene at 50°C emulsified with 0.128 mol dm^{-3} potassium decanoate with 7.40 $\times 10^{-3}$ mol dm^{-3} as initiator. ●, Values estimated from observed values of $\bar{d}_T$; ○, values calculated from Gardon's equation taking the variation of a_S and the concentration of micellar emulsifier with electrolyte concentration

constant, k_d, of potassium persulphate which is applicable under the conditions of emulsion polymerization should be larger than the value[24] adopted by Gardon which is the lowest value which has ever been found, e.g. Brooks and Makanjuola[25] find a fivefold increase in the rate of decomposition in presence of sodium dodecyl sulphate and polystyrene. Although this means that the rate of depletion of initiator is greater than it otherwise would be, it does not necessarily mean that the rate of initiation is also increased. Using the rate of consumption of diphenyl picryl hydrazyl to measure the rate of radical production from persulphate in presence of sodium dodecyl sulphate, polyvinyl alcohol, vinyl acetate, and polyvinyl acetate latex, Dunn and Tonge[26] found no large enhancement of the rate although a twofold increase could not be excluded: Brooks and Makanjuola find a threefold increase in the rate of decomposition in presence of polyvinyl acetate latex. An enhancement of the rate of decomposition of the initiator by a factor of 4.3 (and assuming it to be equal to half the rate of initiation) suffices to bring the calculated particle size into agreement with the observed size when Mahabadi and O'Driscoll's value of k_p is used in Gardon's expression for particle size.

The increase in particle size observed with potassium octadecanoate and with potassium decanoate at the higher electrolyte concentrations (*Figure 5*) cannot be accounted for on the basis of Gardon's equation. It is most probably a result of the effect of electrolyte concentration in increasing the size of the initial micelles. Piirma and Wang[27] find a correlation between the size of the mixed micelles formed when mixtures of an anionic and a non-ionic emulsifier are used and the number of latex particles formed. It is difficult to understand why there should be an effect of micelle size when fewer than one micelle in a hundred ever become the nucleus of a latex particle[2]. The explanation may be that the efficiency with which radicals generated in the aqueous phase are captured is a sensitive function of particle size.

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